Quinolin-8-aminium toluene-4-sulfonate

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The crystal structure of quinolin-8-aminium toluene-4-sulfonate [$(C_9 H_9 N_2)^+ (C_7 H_7O_3S)^-$] is different from previously characterized proton-transfer compounds 8-aminoquinoline in that the 8-amino group rather than the quinoline-N is protonated. All protons of this aminium group are subsequently involved in intermolecular H-bonding interactions with sulfonate oxygen acceptors acting as bridging molecules in a simple linear polymer structure.

Experimental

Crystal data

$C_9H_9N_2·C_7H_7O_3S$
M_r = 316.37
Triclinic, $P\overline{1}$
a = 9.8930 (17) Å
b = 13.424 (2) Å
c = 6.0986 (14) Å
α = 100.783 (16)°
β = 101.401 (16)°
γ = 78.096 (14)°
V = 767.8 (3) Å^3
Z = 2
Mo $K\alpha$ radiation, λ = 0.71069 Å
μ = 0.23 mm^{-1}
T = 298 K
0.40 × 0.20 × 0.18 mm

Data collection

Rigaku AFC 7R diffractometer
4042 measured reflections
3528 independent reflections
2857 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
3 standard reflections every 150 reflections
intensity decay: 0.4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.124
S = 0.83
3528 reflections
212 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1

Selected geometric parameters (Å, º)

S1—O1	1.4517 (19)	N11—C91	1.364 (3)
S1—O2	1.4425 (18)	N11—C21	1.312 (3)
S1—O3	1.4719 (15)	N81—C81	1.464 (3)
S1—C1	1.771 (2)		
O1—S1—O2	114.43 (10)	S1—C1—C6	120.41 (16)
O1—S1—O3	111.40 (9)	S1—C1—C2	119.72 (17)
O1—S1—C1	106.57 (9)	N11—C21—C31	124.4 (2)
O2—S1—O3	111.49 (9)	N81—C81—C91	117.78 (16)
O2—S1—C1	106.98 (10)	N81—C81—C71	120.26 (18)
O3—S1—C1	105.33 (9)	N11—C91—C101	123.18 (16)
C21—N11—C91	116.84 (17)	N11—C91—C81	118.86 (17)

Table 2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N81—H81*A*···O3^{i}	0.95 (2)	1.86 (2)	2.800 (2)	168.6 (19)
N81—H81*B*···O3^{vii}	0.88 (3)	2.14 (3)	2.869 (2)	140 (2)
N81—H81*C*···O1^{ii}	0.97 (3)	1.83 (3)	2.791 (3)	169 (3)
C21—H21···O3	0.9556	2.5883	3.494 (3)	158.34

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, −*y*+2, −*z*+1; (vii) *x*, *y*, *z*−1.

Data collection: *MSC/AFC Diffractometer Control Software*; cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* for Windows (MSC/AFC, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* for Windows (Spek, 1999); software used to prepare material for publication: *PLATON* for Windows (Spek, 1999).

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supplementary materials

Quinolin-8-aminium toluene-4-sulfonate

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Comment

8-Aminoquinoline (8-AQ) is stereochemically similar to 8-hydroxyquinoline (oxine) and would appear to be as useful as 8-AQ for structure extension through hydrogen bonding interactions. However, this is not the case, with only a small number of crystal structures of proton-transfer compounds compared to 8-HQ (Smith, Wermuth & White, 2001) being reported. We have reported the crystal structures of the proton-transfer compounds of 8-AQ with a series of nitro-substituted carboxylic acids (Smith, Wermuth, Bott et al., 2001): 3-nitrobenzoic acid, 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid (all 1:1), and chemically characterized those with 3,5-dinitro-benzoic acid (1:1) and 4-nitrobenzoic acid (a 1:1:1 acid adduct). In all of the crystal structures 8-AQ adopts bridging mode via the quinolinium- and amino-nitrogen groups, linking the acid molcules into linear chains. A 1:1 adduct with Kemp's triacid (cis, cis-1,3,5-trimethylcyclohexane- 1,3-5-tricarboxylic acid) (Smith et al., 2000) which surprisingly is non- transfer, considering the acid strength (pK_{a1} = 1.5). An unstable disordered adduct with 1,3,5-trinitrobenzene (TNB) with formula [$(8\text{-AQ})_{0.8}$ $(TNB)_{0.6}$)] is also known (Smith, Wermuth, Bott et al., 2001). The structure of only one compound with a sulfonic acid, 5-sulfosalicylic acid (a 1:1 dihydrate) is known (Smith et al., 2004), so we undertook the preparation of crystals of aromatic sulfonic acid salts of 8-AQ with the ain of characterizing the hydrogen-bonding patterns in such compounds, but without much success.One exception is the 1:1 proton-transfer compound with 4-toluenesulfonic acid (PTSA) [$(C_9 H_9 N_2)^+$ $(C_7 H_7 O_3 S)^-$] (I). Success with PTSA is unusual, considering that crystal structures of proton-transfer Lewis base compounds with PTSA are uncommon, possibly because of the absence of interactive functional substituent groups to promote secondary hydrogen-bonding extension

The structure determination of (I) shows, as expected, the presence of proton transfer but surprisingly the the acceptor group is the 8-amino substituent rather than the quinoline hetero-N, as has been observed in all previous examples involving quinoline and substituted quinolines (Smith, wermuth, Bott et al., 2001; Smith, Wermuth, Healy et al., 2004; Smith, wermuth %& White, 2004). It was assumed, in the absence of pK_a data for the second dissociation constant for 8-AQ (pK`a1 = 4.0 cf. 4.8 for the hetero-N of quinoline) thatthe amino-N was less basic and should be protonated last. Why? Fig. 1 shows the 8-AQ cation and PTSA anion pair in (I). In (I), all three hydrogen donors of the protonated amine group give direct hydrogen-bonding associations with two of the sulfonate oxygen acceptors from three independent PTSA anion molecules [N81—H81A··· $O3^{i}$, 2.800 (2) Å; N81—H81B···$O3^{ii}$, 2.869 (2) Å; N81—H81C··· $O3^{iii}$, 2.791 (3) Å: symmetry codes; (i) - x, 1 - y , - z ; (ii) x, y, -1 + z; iii - x, 2 - y, 1 - z]. The third sulfonate-O (O2) is not involved, nor is the hetero-N (N11). These associations are the only ones present in the structure and result in the formation of a simple chain polymer, forming down the c cell direction (Fig. 2).

Experimental

The synthesis of the title compound was carried out by heating under reflux for 10 min, 1 mmol quantities of 8-aminoquinoline (8-AQ) and 4-toluenesulfonic acid (PTSA) in 50 mL of 80% ethanol/water. After concentration to ca. 30 mL, partial room temperature evaporation of the hot-filtered solution gave colourless prismatic crystals, m. p. 421.5–425.0 K.

Refinement

Hydrogen atoms of the protonated amine group of 8-AQ (H81A–C) were located by difference methods and their positional and isotropic thermal parameters were refined. Others were included in the refinement at calculated positions as riding models with C—H fixed at 0.95 Å and U_{iso} = 1.2U(C).

(674GS01_PTSAAQ)

Crystal data

$C_9H_9N_2 \cdot C_7H_7O_3S$	Z = 2
M_r = 316.37	F(000) = 332
Triclinic, $P\overline{1}$	D_x = 1.368 Mg m^{-3}
Hall symbol: -P 1	Melting point: 421.5–425.0 K K
a = 9.8930 (17) Å	Mo $K\alpha$ radiation, λ = 0.71069 Å
b = 13.424 (2) Å	Cell parameters from 25 reflections
c = 6.0986 (14) Å	θ = 12.6–17.4°
α = 100.783 (16)°	μ = 0.23 mm^{-1}
β = 101.401 (16)°	T = 298 K
γ = 78.096 (14)°	Prism, Colourless
V = 767.8 (3) Å^3	0.40 × 0.20 × 0.18 mm

Data collection

Rigaku AFC 7R diffractometer	R_{int} = 0.031
Radiation source: Rigaku rotating anode	θ_{max} = 27.5°, θ_{min} = 2.9°
graphite	h = −12→12
ω–2θ scans	k = −17→17
4042 measured reflections	l = −7→3
3528 independent reflections	3 standard reflections every 150 reflections
2857 reflections with $I > 2\sigma(I)$	intensity decay: 0.4%

Refinement

Refinement on F^2	Secondary atom site location: Difference Fourier map
Least-squares matrix: Full	Hydrogen site location: Inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.042	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.124	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.0104P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.83	$(\Delta/\sigma)_{max} < 0.001$
3528 reflections	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
212 parameters	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: Structure-invariant direct methods	Extinction coefficient: 0.019 (3)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All esds are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	−0.10971 (5)	0.79655 (4)	0.60780 (8)	0.0376 (1)
O1	−0.12739 (17)	0.79790 (12)	0.8391 (3)	0.0527 (5)
O2	−0.23467 (15)	0.78809 (13)	0.4424 (3)	0.0581 (5)
O3	−0.04746 (15)	0.88447 (10)	0.5885 (2)	0.0435 (4)
C1	0.01601 (19)	0.68580 (14)	0.5404 (3)	0.0378 (5)
C2	0.0115 (3)	0.6377 (2)	0.3193 (4)	0.0622 (8)
C3	0.1154 (3)	0.5544 (2)	0.2671 (5)	0.0723 (9)
C4	0.2217 (3)	0.51779 (17)	0.4298 (5)	0.0608 (9)
C5	0.2257 (3)	0.5683 (2)	0.6476 (5)	0.0757 (10)
C6	0.1231 (3)	0.6517 (2)	0.7039 (4)	0.0627 (8)
C7	0.3319 (4)	0.4260 (2)	0.3670 (7)	0.0936 (13)
N11	0.18515 (16)	0.89084 (13)	0.1098 (3)	0.0404 (5)
N81	0.12455 (17)	1.03296 (13)	−0.1836 (3)	0.0384 (5)
C21	0.2143 (2)	0.82378 (18)	0.2512 (4)	0.0512 (7)
C31	0.3425 (3)	0.75528 (19)	0.2863 (4)	0.0571 (8)
C41	0.4453 (2)	0.75841 (17)	0.1705 (4)	0.0513 (7)
C51	0.5213 (2)	0.83847 (17)	−0.1110 (4)	0.0490 (6)
C61	0.4908 (2)	0.90746 (19)	−0.2565 (4)	0.0544 (8)
C71	0.3590 (2)	0.97250 (17)	−0.2832 (4)	0.0473 (6)
C81	0.26118 (18)	0.96490 (14)	−0.1615 (3)	0.0352 (5)
C91	0.28744 (18)	0.89359 (13)	−0.0085 (3)	0.0340 (5)
C101	0.42113 (19)	0.82858 (14)	0.0166 (3)	0.0401 (5)
H2	−0.063000	0.661000	0.203800	0.0740*
H3	0.112900	0.521900	0.112300	0.0850*
H5	0.301100	0.545800	0.762800	0.0890*
H6	0.125700	0.684500	0.857900	0.0750*
H7A	0.338100	0.419600	0.209300	0.1120*
H7B	0.308800	0.364500	0.392600	0.1120*
H7C	0.421200	0.434900	0.453400	0.1120*
H21	0.143400	0.820300	0.334200	0.0600*
H31	0.357100	0.707100	0.390200	0.0670*
H41	0.533700	0.713300	0.192700	0.0600*
H51	0.611700	0.795500	−0.093700	0.0570*
H61	0.559700	0.912400	−0.342300	0.0640*
H71	0.338500	1.022100	−0.386100	0.0560*
H81A	0.110 (2)	1.0638 (17)	−0.317 (4)	0.044 (6)*

H81B	0.060 (3)	0.996 (2)	−0.187 (4)	0.058 (7)*
H81C	0.120 (3)	1.087 (2)	−0.054 (5)	0.064 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0324 (2)	0.0378 (2)	0.0423 (3)	−0.0029 (2)	0.0111 (2)	0.0040 (2)
O1	0.0577 (9)	0.0521 (8)	0.0530 (9)	−0.0043 (7)	0.0275 (7)	0.0065 (7)
O2	0.0357 (8)	0.0629 (10)	0.0669 (10)	−0.0052 (7)	−0.0022 (7)	0.0032 (8)
O3	0.0452 (8)	0.0364 (7)	0.0502 (8)	−0.0055 (6)	0.0115 (6)	0.0076 (6)
C1	0.0370 (9)	0.0324 (8)	0.0449 (10)	−0.0057 (7)	0.0117 (8)	0.0034 (7)
C2	0.0526 (13)	0.0663 (15)	0.0520 (13)	0.0011 (11)	0.0034 (10)	−0.0119 (11)
C3	0.0682 (16)	0.0636 (16)	0.0703 (17)	−0.0027 (13)	0.0194 (14)	−0.0251 (13)
C4	0.0584 (14)	0.0346 (10)	0.0915 (19)	−0.0011 (10)	0.0299 (13)	0.0042 (11)
C5	0.0722 (17)	0.0653 (16)	0.0765 (18)	0.0257 (14)	0.0113 (14)	0.0207 (14)
C6	0.0695 (16)	0.0574 (14)	0.0481 (12)	0.0161 (12)	0.0080 (11)	0.0070 (10)
C7	0.082 (2)	0.0469 (14)	0.151 (3)	0.0118 (14)	0.053 (2)	0.0025 (17)
N11	0.0327 (8)	0.0442 (9)	0.0455 (9)	−0.0042 (6)	0.0115 (7)	0.0077 (7)
N81	0.0309 (8)	0.0407 (8)	0.0445 (9)	−0.0007 (6)	0.0102 (7)	0.0108 (7)
C21	0.0436 (11)	0.0601 (13)	0.0564 (13)	−0.0087 (10)	0.0151 (10)	0.0185 (10)
C31	0.0544 (13)	0.0553 (13)	0.0632 (14)	−0.0059 (10)	0.0028 (11)	0.0245 (11)
C41	0.0391 (10)	0.0451 (11)	0.0640 (14)	0.0019 (9)	0.0022 (9)	0.0108 (10)
C51	0.0313 (9)	0.0465 (11)	0.0648 (13)	0.0002 (8)	0.0159 (9)	−0.0028 (10)
C61	0.0392 (11)	0.0648 (14)	0.0633 (14)	−0.0056 (10)	0.0274 (10)	0.0041 (11)
C71	0.0443 (11)	0.0517 (11)	0.0499 (11)	−0.0066 (9)	0.0187 (9)	0.0085 (9)
C81	0.0291 (8)	0.0357 (9)	0.0390 (9)	−0.0042 (7)	0.0087 (7)	−0.0003 (7)
C91	0.0286 (8)	0.0344 (8)	0.0373 (9)	−0.0055 (7)	0.0072 (7)	−0.0006 (7)
C101	0.0301 (9)	0.0376 (9)	0.0482 (10)	−0.0045 (7)	0.0061 (7)	−0.0025 (8)

Geometric parameters (Å, º)

S1—O1	1.4517 (19)	C6—H6	0.9576
S1—O2	1.4425 (18)	C7—H7B	0.9478
S1—O3	1.4719 (15)	C7—H7C	0.9531
S1—C1	1.771 (2)	C7—H7A	0.9625
N11—C91	1.364 (3)	C21—C31	1.409 (4)
N11—C21	1.312 (3)	C31—C41	1.359 (4)
N81—C81	1.464 (3)	C41—C101	1.405 (3)
N81—H81B	0.88 (3)	C51—C101	1.415 (3)
N81—H81C	0.97 (3)	C51—C61	1.350 (3)
N81—H81A	0.95 (2)	C61—C71	1.410 (3)
C1—C6	1.371 (3)	C71—C81	1.360 (3)
C1—C2	1.378 (3)	C81—C91	1.411 (3)
C2—C3	1.389 (4)	C91—C101	1.424 (3)
C3—C4	1.374 (4)	C21—H21	0.9556
C4—C5	1.371 (4)	C31—H31	0.9588
C4—C7	1.513 (4)	C41—H41	0.9567
C5—C6	1.388 (4)	C51—H51	0.9573
C2—H2	0.9588	C61—H61	0.9568
C3—H3	0.9609	C71—H71	0.9636
C5—H5	0.9594		

S1···H81A^{i}	2.81 (2)	C71···C61^{ix}	3.565 (3)
S1···H81C^{ii}	2.88 (3)	C1···H21	2.9740
O1···N81^{ii}	2.791 (3)	C2···H21	2.9848
O2···C41^{iii}	3.336 (3)	C3···H3^{x}	3.0831
O3···N81^{i}	2.800 (2)	C21···H6^{vii}	2.8608
O3···N81^{iv}	2.869 (2)	H2···O2	2.6010
O1···H81C^{ii}	1.83 (3)	H3···H3^{x}	2.4986
O1···H51^{v}	2.6998	H3···H7A	2.3917
O1···H6	2.6418	H3···C3^{x}	3.0831
O2···H41^{iii}	2.7524	H5···H7C	2.5088
O2···H2	2.6010	H6···C21^{iv}	2.8608
O2···H71^{i}	2.6026	H6···O1	2.6418
O2···H81A^{i}	2.83 (2)	H7A···H3	2.3917
O2···H7B^{vi}	2.7256	H7B···O2^{vi}	2.7256
O2···H61^{v}	2.7355	H7C···H5	2.5088
O3···H21	2.5883	H7C···H7C^{xi}	2.4922
O3···H81B^{iv}	2.14 (3)	H21···O3	2.5883
O3···H81A^{i}	1.86 (2)	H21···C1	2.9740
N11···N81	2.754 (3)	H21···C2	2.9848
N11···N81^{i}	3.117 (3)	H41···O2^{viii}	2.7524
N81···O3^{i}	2.800 (2)	H41···H51	2.5434
N81···N11	2.754 (3)	H51···O1^{xii}	2.6998
N81···O1^{ii}	2.791 (3)	H51···H41	2.5434
N81···O3^{vii}	2.869 (2)	H61···O2^{xii}	2.7355
N81···N11^{i}	3.117 (3)	H61···H71^{xiii}	2.4700
N11···H81C^{i}	2.93 (3)	H71···H81A	2.3168
N11···H81C	2.89 (3)	H71···O2^{i}	2.6026
N11···H81B^{i}	2.66 (3)	H71···H61^{xiii}	2.4700
N11···H81B	2.48 (3)	H81A···H71	2.3168
C21···C71^{iv}	3.398 (3)	H81A···S1^{i}	2.81 (2)
C31···C61^{iv}	3.404 (4)	H81A···O2^{i}	2.83 (2)
C31···C71^{iv}	3.548 (3)	H81A···O3^{i}	1.86 (2)
C41···O2^{viii}	3.336 (3)	H81B···O3^{vii}	2.14 (3)
C51···C71^{ix}	3.384 (3)	H81B···N11	2.48 (3)
C61···C31^{vii}	3.404 (4)	H81B···N11^{i}	2.66 (3)
C61···C71^{ix}	3.565 (3)	H81C···N11	2.89 (3)
C71···C31^{vii}	3.548 (3)	H81C···S1^{ii}	2.88 (3)
C71···C21^{vii}	3.398 (3)	H81C···O1^{ii}	1.83 (3)
C71···C51^{ix}	3.384 (3)	H81C···N11^{i}	2.93 (3)

O1—S1—O2	114.43 (10)	C4—C7—H7B	110.70
O1—S1—O3	111.40 (9)	C4—C7—H7C	110.29
O1—S1—C1	106.57 (9)	H7A—C7—H7B	108.60
O2—S1—O3	111.49 (9)	H7A—C7—H7C	108.13
O2—S1—C1	106.98 (10)	H7B—C7—H7C	109.39
O3—S1—C1	105.33 (9)	N11—C21—C31	124.4 (2)
C21—N11—C91	116.84 (17)	C21—C31—C41	119.0 (2)
H81B—N81—H81C	108 (2)	C31—C41—C101	119.5 (2)
C81—N81—H81C	110.6 (18)	C61—C51—C101	120.9 (2)
C81—N81—H81B	108.0 (18)	C51—C61—C71	120.9 (2)
C81—N81—H81A	109.6 (13)	C61—C71—C81	119.4 (2)

H81A—N81—H81B	112 (2)	N81—C81—C91	117.78 (16)
H81A—N81—H81C	109 (2)	N81—C81—C71	120.26 (18)
S1—C1—C6	120.41 (16)	C71—C81—C91	121.95 (18)
C2—C1—C6	119.7 (2)	N11—C91—C101	123.18 (16)
S1—C1—C2	119.72 (17)	N11—C91—C81	118.86 (17)
C1—C2—C3	119.0 (2)	C81—C91—C101	117.96 (17)
C2—C3—C4	122.0 (3)	C51—C101—C91	118.97 (17)
C3—C4—C5	117.9 (3)	C41—C101—C51	124.00 (19)
C3—C4—C7	120.5 (3)	C41—C101—C91	117.03 (17)
C5—C4—C7	121.6 (3)	N11—C21—H21	117.92
C4—C5—C6	121.2 (3)	C31—C21—H21	117.69
C1—C6—C5	120.2 (2)	C21—C31—H31	120.56
C1—C2—H2	120.32	C41—C31—H31	120.42
C3—C2—H2	120.63	C31—C41—H41	120.64
C4—C3—H3	119.25	C101—C41—H41	119.81
C2—C3—H3	118.79	C61—C51—H51	119.78
C4—C5—H5	119.34	C101—C51—H51	119.37
C6—C5—H5	119.51	C51—C61—H61	119.51
C1—C6—H6	119.81	C71—C61—H61	119.59
C5—C6—H6	120.01	C61—C71—H71	120.36
C4—C7—H7A	109.68	C81—C71—H71	120.27

O1—S1—C1—C2	151.18 (19)	N11—C21—C31—C41	1.0 (4)
O1—S1—C1—C6	−33.1 (2)	C21—C31—C41—C101	−0.9 (3)
O2—S1—C1—C2	28.4 (2)	C31—C41—C101—C51	179.6 (2)
O2—S1—C1—C6	−155.97 (19)	C31—C41—C101—C91	0.1 (3)
O3—S1—C1—C2	−90.4 (2)	C101—C51—C61—C71	0.8 (3)
O3—S1—C1—C6	85.3 (2)	C61—C51—C101—C41	179.8 (3)
C21—N11—C91—C81	−179.61 (19)	C61—C51—C101—C91	−0.8 (3)
C21—N11—C91—C101	−0.4 (3)	C51—C61—C71—C81	−0.5 (3)
C91—N11—C21—C31	−0.4 (3)	C61—C71—C81—C91	0.0 (3)
C2—C1—C6—C5	−0.8 (4)	C61—C71—C81—N81	178.9 (2)
C6—C1—C2—C3	0.7 (4)	N81—C81—C91—N11	0.4 (3)
S1—C1—C6—C5	−176.4 (2)	N81—C81—C91—C101	−178.85 (16)
S1—C1—C2—C3	176.4 (2)	C71—C81—C91—N11	179.32 (19)
C1—C2—C3—C4	0.7 (4)	C71—C81—C91—C101	0.1 (3)
C2—C3—C4—C5	−2.1 (4)	N11—C91—C101—C41	0.6 (3)
C2—C3—C4—C7	179.2 (3)	C81—C91—C101—C41	179.75 (18)
C3—C4—C5—C6	2.1 (4)	N11—C91—C101—C51	−178.91 (19)
C7—C4—C5—C6	−179.2 (3)	C81—C91—C101—C51	0.3 (3)
C4—C5—C6—C1	−0.7 (4)		

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, −*y*+2, −*z*+1; (iii) *x*−1, *y*, *z*; (iv) *x*, *y*, *z*+1; (v) *x*−1, *y*, *z*+1; (vi) −*x*, −*y*+1, −*z*+1; (vii) *x*, *y*, *z*−1; (viii) *x*+1, *y*, *z*; (ix) −*x*+1, −*y*+2, −*z*; (x) −*x*, −*y*+1, −*z*; (xi) −*x*+1, −*y*+1, −*z*+1; (xii) *x*+1, *y*, *z*−1; (xiii) −*x*+1, −*y*+2, −*z*−1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N81—H81*A*···O3^{i}	0.95 (2)	1.86 (2)	2.800 (2)	168.6 (19)
N81—H81*B*···O3^{vii}	0.88 (3)	2.14 (3)	2.869 (2)	140 (2)
N81—H81*C*···O1^{ii}	0.97 (3)	1.83 (3)	2.791 (3)	169 (3)
C21—H21···O3	0.9556	2.5883	3.494 (3)	158.34

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, −*y*+2, −*z*+1; (vii) *x*, *y*, *z*−1.

Figure 1

Fig. 1. Molecular configuration and atom numbering scheme for the 8-AQ cation and PASA anion in (I). Atoms are shown as 30% probability ellipsoids

Figure 2

Fig. 2. Packing in the unit cell viewed down b, showing hydrogen-bonding associations as broken lines.